KOSTALEK

Nitrogenous acid derivatives of ethyl malonate

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Ph. D.

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NITROGENOUS ACID DERIVATIVES OF ETHYL MALONATE

BY

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THESIS

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May 24, 1910.

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

John Anton Kostalek

ENTITLED Nitrogenous Acid Derivatives of Ethyl Malonate.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

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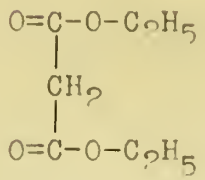
INTRODUCTION.

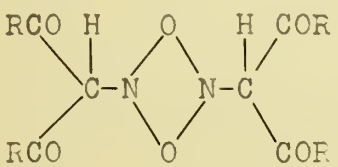
The methylene group situated between two negative groups, as in ethylmalonate,



is very reactive. With nitrogen oxides it reacts readily, with the formation of nitro, nitroso and isonitroso compounds and ketones.

Neufville and Pechmann (1) prepared isonitrosodibenzoylmethane $(C_6H_5CO)_2C{=}NOH$, by the action of methyl nitrite on dibenzoylmethane in the presence of hydrochloric acid.

Wieland and Block (2) obtained two series of derivatives, the bisnitroso compounds,



and 1 ; 2 ; 3 triketones by the action of nitrous anhydride on 1 ; 3 diketones.

Conrad and Bischoff (3) prepared ethyl isonitrosomalonate, $HON{=}C(COOC_2H_5)_2$, by the action of nitrous anhydride on ethyl malonate in the presence of sodium ethylate.

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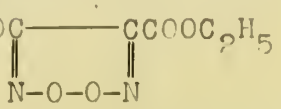
(1). Ber. 23; 3378.

(2). Ber. 37; 1524.

(3). Ann. 209; 211.

Boveault and Wahl (1) made ethyl dinitroacetate, $(NO_2)_2CH\cdot COOC_2H_5$, and bisanhydronitroacetate,



by the action of fuming nitric acid on acid ethyl malonate.

Wahl (2) prepared ethyl nitromalonate, $O_2N\cdot CH(COOC_2H_5)_2$, by the action of fuming nitric acid on ethyl malonate.

By the action of the red oxides of nitrogen on ethyl malonate, Curtiss (3) obtained ethyl dihydoxymalonate, $(HO)_2C(COOC_2H_5)_2$, and an unstable acid oil. This acid oil when treated with alcoholic potash yielded a yellow potassium salt, whose potassium content corresponded to that of ethyl isonitrosomalonate, $KON=C(COOC_2H_5)_2$. Curtiss and Roark (4) found that this oil consisted to a large extent of two components, which they designated as the α and the β acid oils. They prepared metallic derivatives of these oils, but did not establish their identity. They also isolated a crystalline body from the reaction mixture, which was analyzed, but not identified.

In this investigation, we have identified the α oil as ethyl dinitroacetate, $(NO_2)_2CH\cdot COOC_2H_5$, and the β oil as ethyl nitromalonate, $NO_2CH(COOC_2H_5)_2$. The potassium salt

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(1). Compt. Rend. 136; 159.

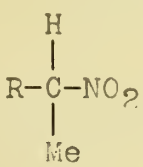
(2). Ibid. 132; 1052.

(3). Am. Chem. Jr. 35; 477.

(4). R. C. Roark, Master's Thesis. University of Illinois. (1908).

of ethyl dinitroacetate was prepared and analyzed. The potassium and ammonium salts of ethyl nitromalonate were also prepared and analyzed. Pure ethyl nitromalonate was made by the action of dilute sulphuric acid on its potassium salt and analyzed.

Victor Meyer, the pioneer investigator in the field of the nitroparaffins, (1) found that these substances yielded salts with alkalies in all cases, where at least one hydrogen was linked directly to the carbon bearing the nitro group. He ascribed this acid property to the negative nature of the nitro group and assigned to these derivatives the general formula,



the metal being linked directly to the carbon.

This view held ground until 1888, when it was combatted by Michaels (2). On the basis of his detailed study of the salt formation in the case of acetoacetic ester and similar compounds, Michaels arrived at the conclusion that the metal is not directly linked to the carbon, but that in the salt formation a rearrangement takes place, the metal linking itself to the more negative oxygen, and he assigned to the metallic

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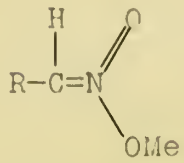
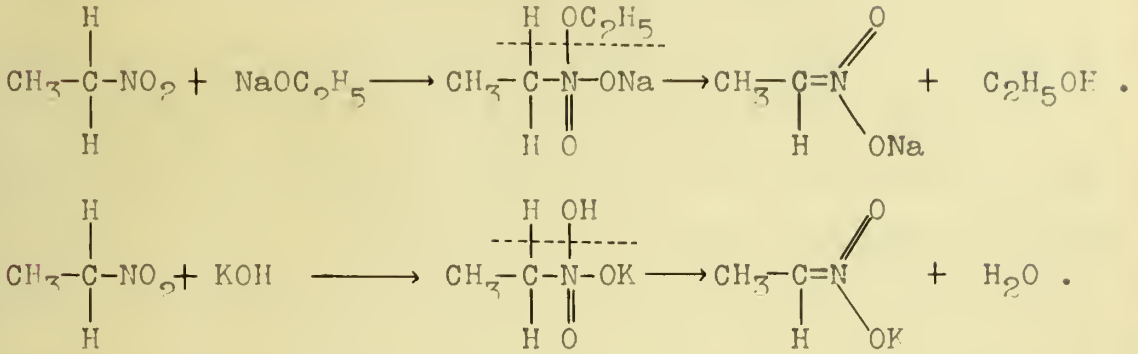
(1). The bibliography and the history of the nitro derivatives is very clearly and fully treated by Henrich in his "Neue Theoretische Anschauungen auf dem Gebiete der Organische Chemie." (page 142).

(2). Jour. f. Pr. Chem. 37 ; 507. (1888).

derivatives the general formula,



In this assumption he was supported by Nef(1), who suggested that the reaction might take place as follows;



The correctness of this assumption was not proven until 1895, when independently and practically simultaneously, Holleman (2) working with phenylnitromethane and nitrobarbituric acid, Hantzsch and Schultze (3) with phenyl nitromethane, and Konowalow (4) with phenyl nitromethane and other nitro derivatives of the arylated fatty hydrocarbons, announced that they had isolated the two isomeric forms, the true nitro body and the isonitro form suggested by Michaels.

This phenomena of desmotropism finds its classical example in the case of phenyl nitromethane.

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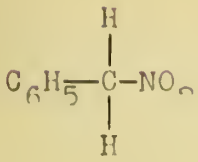
(1). Ann. 280, 263. (1894).

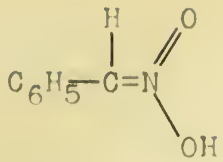
(2). Rec. d. Trav. d. Chem. d. Pays. Bas. 14, 129; 15, 356.

(3). Ber. 29, 2193.

(4). Ibid. 29, 699; 2251.



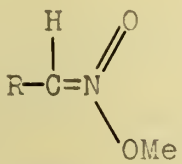
(1) Pseudo Acid



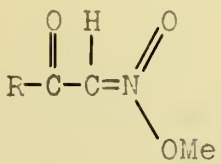
(2) "Aci" Form

The stable liquid form (1) is a true nitro body. The solid labile form (2) is obtained by treating the salts, formed by the action of akalies on phenyl nitromethane with an acid. Hantzsch working chiefly with phenyl nitromethane, has been the most prominent worker in this large and fertile field, and it is to him that we owe most of our present knowledge of these compounds. To the class of compounds, which like phenyl nitromethane derive their acidic properties by a molecular rearrangement, Hantzsch applies the name of pseudo acids. The true acid form he designates as the "aci" nitro body.

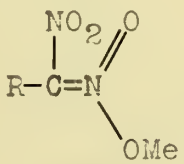
The metallic salts of the "aci" nitroderivatives of the type (1),



(1).



(2).



(3).

as well as those of the nitroketone type (2) and "aci" dinitro type (3) are colorless[1]. Many of the compounds containing groups (2) and (3) are colored. Hantzsch[2] has suggested the color of these compounds is the result of an internal rearrangement. In the nitroketone series (2), he points out that the carbonyl and the nitro group possibly form a union as follows;

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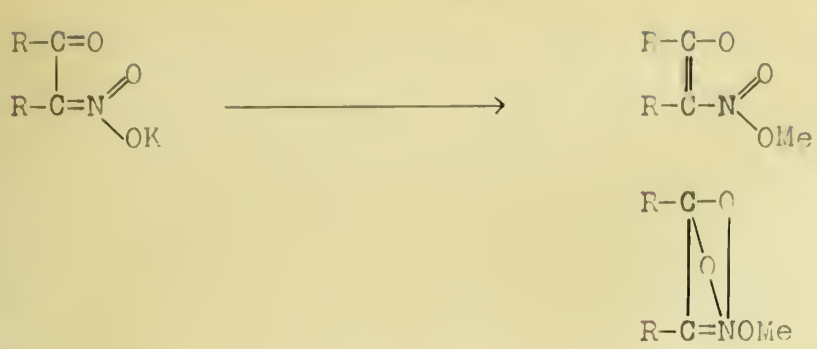
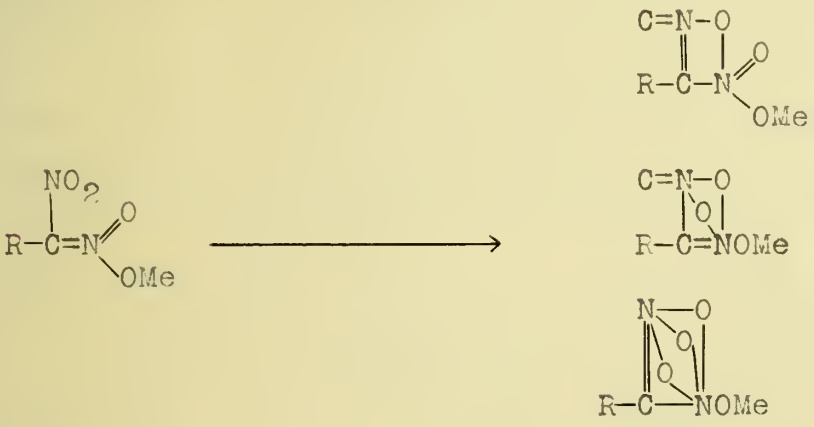
(1). Ber. 40 ; 1533.

(2). Ber. 40 ; 1523; 1533.



leuko form chromo form

In a similar way in the "aci" dinitro series of the type (3) page 5, he suggests that the two nitro groups could undergo the following rearrangement;



leuko form chromo form

While therefore at least three derivatives of this type are possible, only two, the red and the yellow salts are known. In solution these two forms are in equilibrium, the yellow form being stable at ordinary temperatures and the red at higher temperatures. A solution containing the salt of the "aci" dinitro paraffine of this type changes from yellow to red when heated. By the addition of propyl alcohol to the hot aqueous solution of sodium phenyl dinitromethane, Hantzsch (1) obtained

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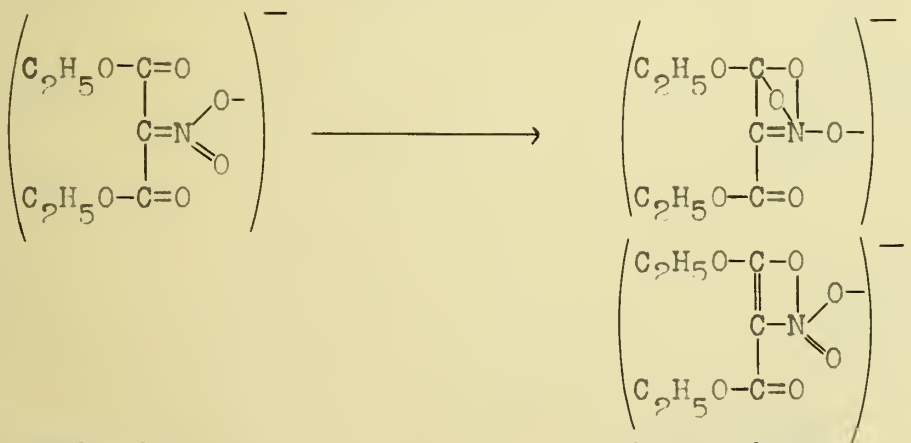
(1). Ber. 40, 1543.

the red modification. When the same solution was allowed to cool the yellow form crystallized out.

The salts of the "aci" derivatives of the nitroketone type are not as highly colored as the salts of the "aci" dinitro paraffines, and only in a very few cases are the two colored modifications, the red and the yellow known. The "aci" derivatives of this series can, in most cases, be easily obtained in the leuko form. Thus ammonium ethyl nitromalonate (1) $H_4NOON{=}C(COOC_2H_5)_2$ can be obtained in the leuko form by recrystallization of the yellow chromo form from absolute alcohol. Dissolved in water or alcohol, the leuko ammonium ethyl nitromalonate yields a yellow solution, indicating that in solution the leuko ion is not stable and changes into the chromo ion,



leuko ion chromo ion

In potassium ethyl dinitroacetate, with two nitro groups and one carbonyl group linked to the same carbon, both types of rearrangement suggested by Hantzsch, are possible, as follows,

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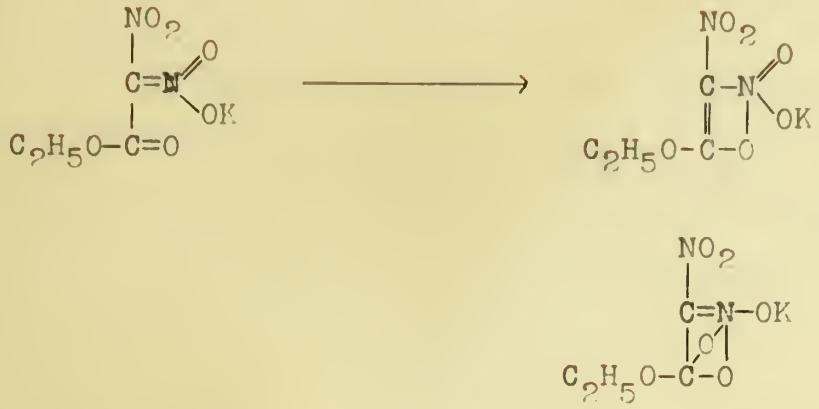
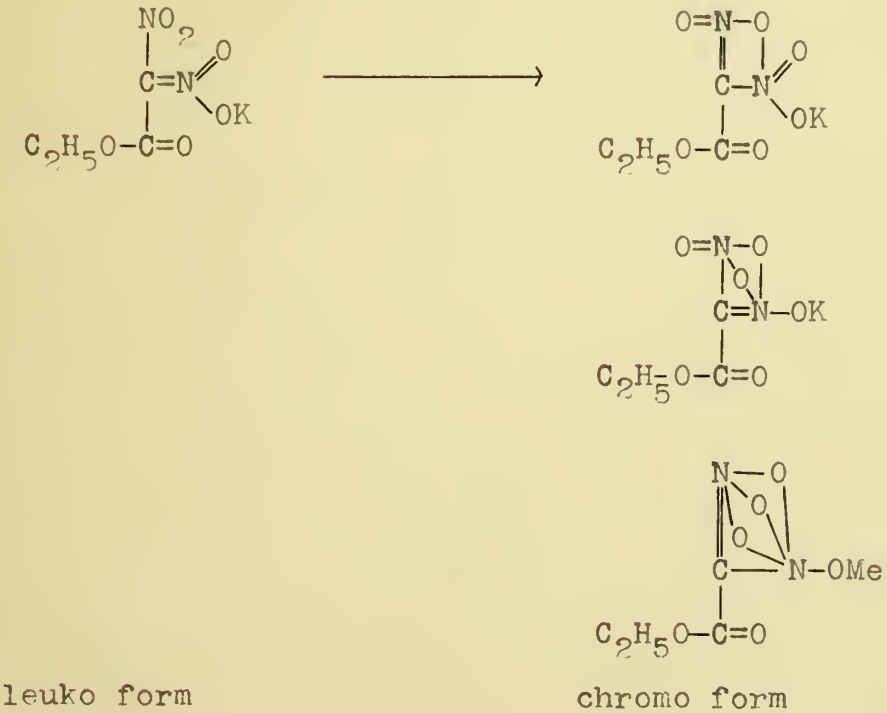
(1). Ber. 40, 1523.

(1).



leuko form chromo form

(2).



leuko form chromo form

A cold aqueous solution of this salt is yellow, but on heating the color changes to reddish brown almost red, while in absolute alcoholic solution the color remains yellow even when the solution is brought to boiling. This may be due to the difference in the degree of dissociation of the salt in these two solvents.

In the preparation of the potassium salts of the acid oils, the first few drops of alcoholic potash, in some cases, produced a deep red coloration, which would suddenly disappear and the precipitation of the yellow potassium salts immediately follow. This coloration is undoubtly due to the temporary formation of the red modification of potassium ethyl dinitro-acetate and potassium ethyl nitromalonate.

EXPERIMENTAL.

PREPARATION OF THE NITROGENOUS ACID OILS BY THE ACTION OF NITROGEN OXIDES ON ETHYLMALONATE.

The oils were prepared according to the method used by Curtiss.(1).

A stream of nitrogen oxides, prepared by the action of nitric acid, sp. gr. 1.42, on arsenious oxide, was passed into 50 cc. of malonic ester kept at -10° to -15°. In twenty minutes the ester had increased 88 grs. in weight. It was then packed in ice and allowed to warm slowly, over a period of seventeen hours, to room temperature. The color of the solution had changed from a dark blue to a light emerald green. A current of air was passed through it for twenty minutes, with but very little loss of dissolved gases. The solution was then placed in a freezing mixture and on shaking an abundant crystallization of ethyl dihydroxy malonate took place. These crystals were filtered off and found to weigh 20 grs.

The filtrate, a thick, light green oil, possessed a very pungent odor and was very irritating to the eyes. It was washed twice with 100 cc. of water at 0°. The aqueous wash removed the substance possessing the pungent odor almost completely. The oil was then dissolved in 25 cc. of ether, and dried over anhydrous sodium sulphate for two hours. After evaporating the ether over sulphuric acid in a vacuum dessicator, 23 grs. of a light greenish oil of a high specific gravity remained.

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(1). Am. Chem. Jr. 35; 479.

PREPARATION OF THE POTASSIUM SALTS OF THE ACID OILS.

These salts were prepared according to the method of Curtiss and Roark. (1).

Twenty grams of the acid oils, prepared as described above, was dissolved in 125 cc. of absolute alcohol, cooled to -8° to -10° and 46 cc. of absolute alcoholic potash (.14 grs. of potassium hydroxide per cc.) were added drop by drop by means of a separatory funnel. The first drop of alcoholic potash precipitated a yellow crystalline salt. In some experiments the first few drops of alcoholic potash produced a red coloration, which would suddenly disappear and the precipitation of the yellow salt immediately follow. It was also noted by Curtiss and Roark (2) that when alcoholic potash was added to the distilled acid oils, the first drop precipitated a white salt, while further addition of alcoholic potash precipitated a yellow salt. During the addition of the alcoholic potash the solution must be continually shaken. A large amount of heat was liberated in this reaction and if the temperature was allowed to rise, the potassium salt was precipitated in the form of a gummy mass very difficult of purification. The salt was filtered off and washed with absolute alcohol to remove the excess of alkali or any unchanged oils and dried in a vacuum dessicator. Nineteen grams of a yellow salt were obtained.

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(1) R. C. Roark, Master's Thesis, University of Illinois. (1908) page 5.

(2). Ibid. page 4.

SEPARATION OF THE POTASSIUM SALTS OF THE ACID OILS.

SEPARATION OF POTASSIUM ETHYL DINITROACETATE.

Thirty-three grams of the yellow potassium salts, prepared as just described, were dissolved in 60 cc. of hot water. The solution was reddish brown when hot, becoming greenish yellow when cold. On cooling the potassium salts crystallized out in the form of green-yellow needles. These were filtered off, washed with 15 cc. of absolute alcohol and 5 cc. of ether. Yield 17 grs. Decomposing Point 190°. This was practically pure potassium ethyl dinitroacetate.

On recrystallizing it three times from hot 95% alcohol, it was obtained in the form of green-yellow almost colorless needles with a constant decomposing point of 194° - 195°, when immersed in the bath at 190°. It was finely powdered, dried over sulphuric acid in a vacuum dessicator, and analyzed. On prolonged exposure to light the color changes to a darker yellow.

0.1905 grams substance yielded 0.1578 grams of carbon dioxide and 0.0463 grams of water.

0.1805 grams substance yielded 0.1497 grams of carbon dioxide and 0.0432 grams of water.

0.2059 grams substance yielded 0.0828 grams potassium sulphate.

0.2458 grams substance yielded 0.0989 grams potassium sulphate.

0.2086 grams substance yielded 25.2 cc. nitrogen at 25.5 and 734 mm.

0.2198 grams substance yielded 27.0 cc. nitrogen at 28 and 745 mm.

	Calculated for $C_4H_5N_2O_6K$. per cent	Found per cent	
K	18.05	18.06	18.01
H	2.31	2.70	2.65
N	12.96	13.24	12.96
C	22.22	22.62	22.52

The analysis of this salt is very difficult because of the rapidity with which it decomposes when heated.

Curtiss and Roark (1) determined the molecular weight of this salt by the boiling point method, using acetone as a solvent and by the freezing point method, using water as a solvent. These determinations show that it is monomolecular.

Heated on a platinum spatula it explodes violently. When heated gradually in a test tube, the salt chars and a heavy oil condenses at the upper end of the tube. This oil suddenly explodes, bursting into flame.

The aqueous solution, as well as a solution of this salt in 95% alcohol, changes color on heating, but no such change was observed in solutions of the salt in absolute alcohol.

In several instances potassium ethyl dinitroacetate crystallized from aqueous solution in glistening plates, but on recrystallization it crystallized in needles again.

SEPARATION OF POTASSIUM ETHYL NITROMALONATE.

The filtrate from the potassium ethyl dinitroacetate

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(1). R.C.Roark, Master's Thesis. University of Illinois. (1908) page 10.

containing the remainder of the potassium salts was evaporated to one half its volume, and a second crop of crystals, melting at 148° to 149°, was obtained. This crop consisted principally of potassium ethyl nitromalonate, but also contained some potassium ethyl dinitroacetate. An attempt was made to seperate the potassium ethyl nitromalonate by recrystallization from 95% alcohol. By this method a beautiful yellow salt, which had a constant melting point of 145° to 146° was obtained. When analyzed it was found to be impure.

Seven grams of the salt melting at 145° was recrystallized four times from absolute alcohol, using 50 cc. of the solvent to 1 gr. of the salt. Three grams of a yellow salt, crystallizing in small glistening plates and melting at 154 was thus obtained. This was finely powdered, dried in a vacuum dessicator over sulphuric acid, and analyzed.

0.19545 grams of the substance yielded 0.06975 grams of potassium sulphate.

0.20945 grams of the substance yielded 0.07340 grams of potassium sulphate.

0.24995 grams of the substance yielded 0.3190 grams of carbon dioxide, and 0.0912 grams of water.

0.2462 grams of the substance yielded 0.30635 grams of carbon dioxide, and 0.0927 grams of water.

0.2101 grams of the substance yielded 11.9 cc. of nitrogen at 26 and 727 mm.

0.2243 grams of the substance yielded 12.5 cc. of nitrogen at 23.5 and 730 mm.

	Calculated for $C_7H_{10}NO_6K$. per cent	Found per cent	
K	16.04	16.02	15.76
N	5.76	6.02	6.09
C	34.52	34.47	34.80
H	4.12	4.02	4.19

ACTION OF ALKYL HALIDES ON POTASSIUM ETHYL DINITROACETATE.

Potassium ethyl dinitroacetate does not react with ethyl or methyl iodide in the presence of 95% alcohol or absolute alcohol to any appreciable extent, even if heated in a sealed tube to 145° to 150°. In the presence of 50% alcohol a reaction did take place. Equimolecular quantities of potassium ethyl dinitroacetate and methyl,as well as ethyl iodide were heated with 50% alcohol in a sealed tube for one hour at 100° to 110°. By extraction of the reaction mixture with ether, a yellow viscous oil was obtained, which did not crystallize. This oil was formed to the extent of 20% of the potassium salt used. It was not further studied, because of the ease with which it decomposed when any attempt was made to purify it.

ACTION OF ETHYL SULPHATE ON POTASSIUM ETHYL DINITROACETATE.

Potassium ethyl dinitroacetate reacted more readily with ethyl sulphate than with alkyl halides.

Equimolecular quantities of potassium ethyl dinitroacetate and ethyl sulphate were heated for thirty minutes in a sealed tube to 100° to 110° with 50% alcohol. Potassium sulphate and potassium nitrite were formed in the reaction. On extraction with ether a heavy oil was obtained. This oil is formed to the extent of 50% of the potassium salt used. It did not crystallize

and on distillation under diminished pressure it was found to be a mixture of four oils, which were not further studied because of lack of time.

ACTION OF ALCOHOLIC POTASH ON POTASSIUM ETHYL DINITROACETATE.

Equimolecular quantities of potassium ethyl dinitroacetate and absolute alcoholic potash were heated with 99% alcohol over a boiling water bath with a reflux condenser. A chrome yellow salt was obtained, decomposing with explosive violence at 206° to 208°. When recrystallized twice from 70% alcohol, it was obtained in the form of flat light yellow needles decomposing explosively at 208° to 210°.

In the determination of the decomposing point the ordinary melting point apparatus was used and in several cases the capillary tube was blown through the bottom of the flask.

The salt was not obtained pure. Potassium and nitrogen determinations indicate that the chrome yellow salt is not potassium potassium dinitroacetate. This salt is being studied.

The free acid liberated by the action of acids on this salt decomposes spontaneously with explosive violence and the evolution of a large amount of heat.

REDUCTION OF POTASSIUM ETHYL DINITROACETATE.

Potassium ethyl dinitroacetate was submitted to the reducing action of dilute hydrochloric acid and granulated tin. The reaction mixture was extracted with ether and a heavy yellow viscous oil was obtained. This oil reduced Fehling's solution. With concentrated sulphuric acid and an aqueous solution of egg albumen (1), it yielded a pink-purple solution, indicating the presence of glyoxylic acid. The aqueous extract was treated

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(1). Hopkins-Cole Reaction.

with hydrogen sulphide to remove the dissolved tin. The residue, obtained by the evaporation of the aqueous extract, when heated with potassium hydroxide, yielded ammonia, indicating the presence of ammonium salts. No hydroxylamine or hydrazine was found in the residue.

The action of reducing agents on potassium ethyl dinitro-acetate is being studied at the present time.

THE PREPARATION OF ETHYL NITROMALONATE FROM POTASSIUM ETHYL NITROMALONATE.

Fifteen grams of finely powdered potassium ethyl nitromalonate was suspended in 100 cc. of ether and 10 cc. of water added. On shaking, the salt dissolved completely in the aqueous layer. By means of a dropping funnel 3.24 grams of sulphuric acid, dissolved in 50 cc. of water, was added at the rate of about a drop per second, the solution being continually agitated and kept cool by immersion in ice water. The potassium salt, which had crystallized out when the solution was placed in ice water, dissolved rapidly, the aqueous layer changing in color from a bright yellow to a pale yellow. The solution was then taken out of the ice water and allowed to warm slowly to room temperature (20°), agitation of the solution being continued. The aqueous solution was extracted four times with 40 cc. of ether.

The pale yellow ethereal extract was washed four times with 40 cc. of water- these aqueous washes were all distinctly yellow. It was shaken with a little sodium carbonate solution to remove any free sulphuric acid present. The sodium carbonate imparted to the almost colorless ethereal extract a golden yellow color. This coloration was due to the formation of the "chromo" sodium salt of

ethyl aci-nitromalonate. It was then washed twice with 20 cc. of water and dried over anhydrous sodium sulphate for twelve hours. A solution with only a slight yellowish tinge was obtained. The ether was evaporated by passing a stream of dry air under diminished pressure through the solution and a light, turbid oil, containing several small crystals was obtained.

This oil was immediately distilled under diminished pressure. Three fractions were collected.

Fraction	Boiling Point	Temperature of bath	Pressure	Yield	Remarks
No. 1.	60° to 145°	185° to 190°	33 mm.	.5 gr.	colorless oil
No. 2.	145° to 150.5°	190° to 195°	33 mm.	6.5 gr.	colorless oil
No. 3	last few drops at 150.5°	190° to 195°	33 mm.		Yellow oil

The residue consisted of a small amount of yellow oil containing several crystals.

Fraction No. 2 was redistilled under diminished pressure. Three fractions were collected.

Fraction	Boiling Point	Temperature of bath	Pressure	Yield	Remarks
No. 1.	140° to 152°	190° to 200°	37 to 38	1.5 gr.	colorless oil
No. 2.	152° to 154° mostly 153°	190° to 200°	37 to 38	2.5 gr.	colorless oil
No. 3.	154° to 156.5°	190° to 200°	37 to 38	1.4 gr.	colorless oil

The residue consisted of a small amount of yellow oil.

Fraction No. 2 was submitted to analysis.

0.3403 grams of the substance yielded 0.5177 grams of carbon dioxide.

0.2469 grams of the substance yielded 0.3768 grams of carbon dioxide and 0.1310 grams of water.

0.3372 grams of the substance yielded 20.9 cc. of nitrogen at 25.3 and 741.9 mm.

0.3597 grams of the substance yielded 22.7 cc. of nitrogen at 26.2 and 739.01 mm.

	Calculated for $C_7H_{11}O_6N$. per cent	Found per cent	
C	40.97	41.45	41.60
H	5.36		5.87
N	6.82	6.81	6.85

Ethyl nitromalonate is a clear colorless liquid, heavier than water and possessing a fruit-like odor.

PREPARATION OF THE AMMONIUM SALT OF ETHYL NITROMALONATE.

1.17 grams of ethyl nitromalonate (Fraction No. 2. B.P.153° to 154°, at 37 to 39 mm.) was dissolved in 20 cc. of ether, dried over calcium chloride, and ammonia gas, dried over potassium hydroxide, was passed into it. The ethereal solution was cooled by immersion in a freezing mixture at -9°. When the ammonia gas entered the ethereal solution it immediately precipitated an ammonium salt. The passage of ammonia gas was continued until no further precipitation occured. The salt was filtered off and washed with 20 cc. of dry ether. One gram of a very light yellow flaky salt was obtained. It was recrystallized twice from hot absolute alcohol, using 20 cc. of the solvent to one gram of the substance. The crystallization was rendered more complete by the addition of an equal volume of ether. .5 grams of a very light yellow almost white salt was obtained, which crystallized in long prisms. Melting Point 151°.

0.1717 grams of the substance yielded 22.0 cc. of nitrogen at 22.3 and 739.9 mm.

	Calculated for $C_7H_{14}N_2O_6$. per cent	Found per cent
N	12.61	12.77

Fractions No. 1 and No. 2, obtained in the preparation of nitromalonic ester for analysis, were treated with ammonia gas, as in the preparation of ammonium ethyl nitromalonate. The ammonium salt thus obtained was extracted with cold absolute alcohol, using 100 cc. of the solvent to 1 gram of the substance, and the dissolved salt precipitated by the addition of a volume of ether equal to twice the volume of alcohol used. This method was used for the purpose of removing the ammonium salt from the less soluble impurities. Furthermore, in hot alcoholic solution the ammonium salt decomposes with an evolution of ammonia. By using cold alcohol this decomposition is prevented. The ammonium salt was obtained pure white, crystallizing in the form of long prisms. Melting Point 151.5° to 152°. It was finely powdered, dried in a vacuum dessicator over sulphuric acid and analyzed.

0.1495 grams of the substance yielded 17.5 cc. of nitrogen at 24 and 740.2 mm.

	Calculated for $C_7H_{14}N_2O_6$. per cent	Found. per cent
N	12.61	12.80

The ammonium salt decomposes on standing over sulphuric acid in a vacuum dessicator. Even when pure, it will dissolve in absolute alcohol, forming a yellow solution.

ACTION OF NITROGEN OXIDES ON ETHYL NITROMALONATE.

A stream of the oxides of nitrogen, prepared as above described, and dried over phosphorus pentoxide, were passed into 1.6 grams of ethyl nitromalonate, which was immersed in a bath at -20°. The ethyl nitromalonate turned green as soon as the nitrogen oxides came in contact with it, the temperature rising rapidly and it was only by means of vigorous agitation that the temperature was kept between 0° and -5°. In twelve minutes it had increased 26 grams in weight. It was then packed away in ice for twenty four hours, during which time it lost 3 grams in weightand the small number of crystals it contained when put away were found to have slightly increased in number. Twenty grams of dissolved nitrogen oxides were removed by passing a current of dry air through the solution at 0°. The solution was then distilled under diminished pressure. 9 grams of a clear colorless liquid, boiling at 152° to 154° at 32 mm., was obtained. When treated with alcoholic potash this oil yielded a yellow potassium salt similar in crystalline structure and appearence to potassium ethyl nitromalonate. The boiling point and the appearence of the potassium salt, identify this oil as unchanged ethyl nitromalonate. As has already been stated, when the acid oils are distilled, or when the saturated ethyl malonate warms up too quickly ethyl dinitroacetate is formed, apparently, at the expense of the ethyl nitromalonate.We have not yet found the exact experimental conditions necessary for this reaction to take place. The action of nitrogen oxides on ethyl nitromalonate, especially, in the presence of water, will be studied further.

This experimental work is not yet complete. The esterification of ethyl dinitroacetate and ethyl nitromalonate with aryl halides and the action of reducing agents on the salts of these two derivatives will be studied.

In closing, I wish to express my thanks to Dr. R. S. Curtiss for the suggestions given me during the course of this research.

Organic Laboratory,
University of Illinois,
May 15, 1910.

John Anton Kostalek,
in conjuction with
Dr. R. S. Curtiss.

Biographical.

John Anton Kostalek graduated from the University of Wisconsin in 1907 with the degree of Bachelor of Arts. He received a scholarship in chemistry in the University of Wisconsin for the year 1907-1908 and obtained the degree of Master of Arts in 1908 from that institution. The following two years he held a fellowship in chemistry in the University of Illinois.

He is a member of Phi Beta Kappa, Phi Lambda Upsilon, Sigma Xi and the American Chemical Society.